BIODEGRADABLE FOAM MOULDINGS OF THERMOPLASTIC STARCH

Patent Number:	WO9851466
Publication date:	1998-11-19
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Requested Patent:	WO9851466
Application Number:	WO1998NL00285 19980518
Priority Number (s):	NL19971006079 19970516
IPC Classification:	B29C44/00; C08L3/00
EC Classification:	B29C67/22D1, C08J9/12D, C08J9/232
Equivalents:	AU7676798, NL1006079C
Cited Documents:	CH679564; EP0707034; WO9515894

Abstract

A method is described for producing foam mouldings of a biodegradable thermoplastic polymer, in particular starch, which involves the polymer being fused at elevated temperature in the presence of water and being made into thermoplastic granules/pellets, the granules/pellets being introduced into a mould and being foamed by electromagnetic radiant energy being supplied.

Description

BIODEGRADABLE FOAM MOULDINGS OF THERMOPLASTIC STARCH
The invention relates to the production of three-dimensional foam mouldings which are made of a thermoplastic polymer, in particular a biopolymer such as starch, and which can be used as a biodegradable packaging and filling material.

Foam materials for disposable packaging and filling purposes have the reputation of being damaging to the environment. Recycling of such materials has not, as yet, taken off to any significant degree, because of the low density (and therefore high transportation costs) of these materials. The use of biodegradable foam materials in these applications is therefore a sensible alternative.

WO 92/02559 describes a method for extruding and injection-moulding thermoplastic starch. The mouldings thus obtained have a high density, i.e. more than 1000 kg/m3, whereas 10-100 kg/m3 is desirable for foam products for packaging, and involve high production costs (long cycle times) in the case of thick-walled products.

WO 96/07693 discloses a starch foam which is obtained by extrusion of starch, the foamed sheets obtained then being glued together into panels. This is a labour-intensive method, which moreover does not provide complete freedom with regard to ultimate shape.

According to WO 95/15894, thin-walled mouldings such as wafers, cups and the like are produced from thermoplastic starch by a mixture of 15-40 wt% of starch, 48-65 wt% of water and other constituents such as release agents and vegetable fibres being heated to 155-200"C. This method does not lend itself to the production of thick-walled mouldings as desired, for example, for packaging and filling applications.

According to EP-A-707034, foam mouldings are obtained from a mixture of starch, rubber latex or poly (vinyl alcohol), and water, which is first extruded, is then granulated and finally brought into the desired shape in a mould with heating to 150-250"C. These high temperatures are a drawback, certainly for thick-walled products. In addition, supplying thermal energy (heat) results in non-homogeneous heating, if relatively large particles (pellets and the like) to be foamed are processed.

CH 679564 describes a method for sheet extrusion and/or of profile extrusion of starch or derivatives (crosslinked with melamine) thereof in the form of a moving gel, followed by expansion of the resulting sheet by means of electromagnetic radiation. This manner of processing can lead to foamed sections (so-called 2l/z-D products), but does not provide complete freedom with regard to the ultimate shape of the foam moulding.

There is therefore a need for foam mouldings which are completely biodegradable and can, under mild conditions, be made into any desired threedimensional shape, and for a method for the preparation of these.

A method has been found which meets this need, said method involving the manufacture in a rapid, semi-continuous process, of foam mouldings of a biodegradable thermoplastic polymer by melting the polymer at elevated temperature in the presence of a substance having a permanent dipole (such as water or an alcohol) and being made into unfoamed thermoplastic granules or pellets, the granules or pellets being introduced into a mould and being foamed, said method being characterized in that the granules are foamed in the presence of a plasticizer and/or an adhesion promoter and being welded together by electromagnetic radiation energy being supplied. This way of foaming is found to result in a rapid, homogeneous manner of heating.

Particularly suitable as biodegradable thermoplastic polymer, in particular, is thermoplastic starch, i.e. melt-processable starch. This starch is derived, for example, from potatoes, peas, wheat, rice, maize or tapioca and is used as such or mixed with other biodegradable polymers such as cellulose (derivatives), other polysaccharides such as guar gum, locust bean flour, tragacanth, pectin, gum arabic or other gums, natural rubber, polyesters such as poly(caprolactone) and poly(lactic acid), proteins such as gluten and casein. Proteins and starch can also be added together in the form of flour. The other polymers can amount to up to 75 wt% of the mixture. The thermoplastic starch can be based on native starch or alternatively on physically or chemically modified starch. Physically modified

starch inter alia comprises starch modifications which are produced by ion exchange (e.g. Na+, K+, Ca++). Chemically modified starch and starch derivatives comprise oxidized, carboxymethylated, hydroxyalkylated starch and starch derivatized in some other way.

The starch is preferably admixed with a plasticizer such as a polyol (glycol, diethylene glycol or another alkylene glycol or polyalkylene glycol, glycerol, glycerol monoester, and the like), citric acid ester or a sugar polyol (for example sorbitol, lactitol) or (oligo)saccharide (for example glucose, sucrose, maltose and oligomers such as inulin and maltodextrins), but water on its own may also be sufficient. The amount of water can be, for example, 2.5-40 wt%, in particular 3-35 wt% based on the total of degradable polymer. The amount of additional plasticizer such as glycerol is preferably 0-25 wt%, in particular 1-15%. The polymer can further be admixed with an emulsifier such as lecithin or a monoglyceride, a release agent such as an oil (for example castor oil), a fatty acid or metal salt thereof (e.g. calcium stearate), a natural fibre such as flax or cellulose and/or a filler such as lime or chalk. Other possible additives are colorants, preservatives and in particular swelling or blowing agents such as sodium bicarbonate and nucleating substances such as talc. In addition, the composition can comprise mineral salts such as NaCl in an amount of, for example, 5-15%, which allow drastic modification of the foam structure.

The polymer can be made into granules/pellets in accordance with granulating or pelleting processes known per se, for example by extrusion in a twin-screw extruder at elevated temperature (60-180"C, in particular 100-150"C). The size of the granules is determined by the granulation rate and any grinding steps after granulation.

Depending on the presence of other plasticizers, the water content during extrusion can vary from 3 up to, for example, 35 wt% or 40 wt%. During this extrusion step, starch undergoes a transition from a highly ordered structure to a random, amorphous structure (destructuring).

The granules/pellets obtained can be conditioned to a moisture content that is optimal for the process. Depending on the content of other plasticizers, the moisture content after conditioning varies between 4 and 30%, in particular between 5 and 25%. Then the granules/pellets are introduced into a mould having the shape of the foam product ultimately to be manufactured. The granules can be admixed with a quantity of adhesive, to promote welding together of the granules during foaming.

This adhesive can comprise a plasticizer or a combination of plasticizers, for example glycerol or an oligo- or polysaccharide (e.g. starch, hydrolysed starch or starch physically or chemically modified in some other way, inulin) or a protein or peptide such as gluten or casein or a hydrolysate thereof. Mixtures of such adhesives, such as a mixture of glycerol and enzymatically split or native starch, are likewise suitable. It is also possible to use biodegradable polyesters having a low melting point (< 100"C) such as poly(caprolactone) as adhesives. The amount of adhesive is preferably between 1 and 15%; the total amount of adhesive and plasticizer is preferably 2-20%. The adhesive is preferably applied to the outside of the granules prior to foaming. This can be done by direct application, but also by coating from a solution or emulsion. It is also possible, however, to add the adhesive before the extrusion step.

Foaming takes place with the use of electromagnetic radiation, in particular radiation in the microwave range (frequency between 20 MMz and 10 GMz and in particular between 50 MMz and 5 GHz). In the process, use is made of the radiant energy absorption of the substance having a permanent dipole, such as water or glycerol, said substance heating up in a very short time and passing into the vapour state. In the case of water this involves two processes: - The separate granules/pellets are foamed as a result of the evaporation of water or the other dipole-containing substance. An advantage of this is that no thermal energy has to be supplied from outside. The exact boiling temperature of the dipolar substance depends on the local air pressure. If necessary, the foaming process can be promoted by the presence of blowing agents.

- The loose granules/pellets are simultaneously "welded" together to form a three-dimensional foam moulding. For this to happen it is important that the outside of the granules is fusible, a requirement for this being an at least partially thermoplastic behaviour of the polymer, and/or an adhesion promoter can be used.

It was found to be important for the foaming process to proceed rapidly, i.e.

within a few seconds. This can be achieved by using a microwave source having a high output (up to, for example, 50 kW) or by a combination of a microwave generator and a mould, in which the pressure can be varied rapidly.

After the desired foam shape has thus been imparted to the polymer, the mould is opened and the product is removed.

The foamed products obtained by means of the method according to the invention can have any desired shape. An important application is the use as a packaging medium, for example for vulnerable equipment, glassware, postal items and the like. Alternatively, the foam product can have the shape of beads, discs and the like, which can be used as a filling medium in packaging. The density of the product obtained is generally between 5 and 200 kg/m3, in particular between 10 and 100 kg/m3. Further advantages of this foamed material are the inherently antistatic behaviour, the fact that water-soluble variants are possible and the biodegradability and compostability.

Example 1
A mixture of 100 parts by weight of wheat starch and 10 parts by weight of lime is extruded at 1500C in a counter rotating twin-screw extruder after the addition of water to a total moisture content of 37.5%. In a conditioning step, the granules obtained are brought to a moisture content of 15-16 wt%. The conditioned granules are admixed with 5 wt% of a 50/50 mixture of enzymatically split starch and glycerol.

The granules are introduced into a cylindrical mould (diameter 6 cm, length 6 cm) in a microwave oven with a frequency of 2.45 GHz. After 60 seconds the granules have expanded to a density of the foam product of 150 kg/m3. The product has firmly fused together, with an average cell size of 1.0-1.5 mm.

Example 2
Example 1 is repeated, except that 10 parts by weight of sodium chloride are used instead of lime. Density: 150 kg/m3; average cell size: 0.5-0.8 mm.

Examples 3 and 4
Examples 1 and 2 are repeated, except that no adhesive is used. Density 3 (with lime): 175 kg/m3; 4 (with sodium chloride): 160 kg/m3. In both cases, the spheres have not entirely welded together.

Claims

Claims

1. A process for producing foamed mouldings of a biodegradable thermoplastic polymer, the polymer being molten at elevated temperature in the presence of a substance having a permanent dipole and being made into unfoamed thermoplastic granules/pellets, the granules/pellets being introduced into a mould and being foamed, characterized in that the granules/pellets contain a plasticizer and/or an adhesive and in that the granules/pellets are foamed in one step to give a three-dimensional product by electromagnetic radiation energy being supplied.

2. A process according to Claim 1, wherein the thermoplastic polymer is starch, optionally combined with a natural rubber, polyester, another polysaccharide or protein.

3. A process according to Claim 1 or 2, wherein the electromagnetic radiation has a frequency of between 20 MMz and 10 GHz.

4. A process according to any one of Claims 1-3, wherein the polymer is made into the unfoamed granules/pellets by extrusion.

5. A process according to any one of Claims 1-4, wherein the granules/pellets, just before foaming, contain 5-25 wt% of water.

6. A process according to any one of Claims 1-5, wherein the granules/pellets additionally contain a blowing agent such as a bicarbonate.

7. A process according to any one of Claims 1-6, wherein the granules/pellets additionally contain a plasticizer such as glycerol.

8. A process according to any one of Claims 1-7, wherein the granules/pellets additionally contain a mineral salt such as sodium chloride.

9. A process according to any one of Claims 1-8, wherein the substance having a permanent dipole comprises water.

10. A process according to any one of Claims 1-9, wherein the granules/pellets are admixed with an adhesive such as glycerol and/or a carbohydratc.

11. A moulding of foamed thermoplastic polymer, obtainable by means of the process according to any one of the preceding claims.